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IMPROVED METHOD FOR THE SELECTIVE HYDROGENATION OF NAPHTHALENE TO
TETRAHYDRONAPHTHALENE

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The present invention relates to a novel catalytic formula which is useful in many applications, such as, for example, in the hydrogenation, dehydrogenation, hydroformylation and isomerization of organic compounds. More specifically, the invention relates to catalytic systems of the Ziegler type.

The object of the present invention is to describe a novel catalytic formula which presents a very high activity and a very high selectivity in the partial hydrogenation of naphthalene to tetrahydronaphthalene in the liquid phase.

The catalytic hydrogenation of naphthalene is known in the art. Thus, Raney nickel and nickel salts reduced by the aluminum reducing agent of the Ziegler type have already been used. The results in terms of activity and selectivity are similar to either one of the catalysts. This similarity is due to the partial or total heterogeneity of the catalysts obtained to date with the systems of the Ziegler type. Thus, French Patents 1367 202 and 1390 570 describe the preparation of finely divided catalysts. The performance of the catalysts described in these two patents are thus very limited by the preparation procedure used.

It has been found, and this is the object of the present patent, that one can improve the performance of the Ziegler catalysts, in terms of activity and selectivity in the hydrogenation of naphthalene, by reducing the metal derivative with the organoaluminum derivative in the presence of a third constituent: tetrahydronaphthalene. The resulting catalyst is then soluble in the medium, and the performance of the novel catalytic system so obtained is surprisingly, improved.

The term metal derivative denotes any salt of metals of group VIII, which is soluble in tetrahydronaphthalene at the preparation temperature of the catalysts. For example, one can cite the CO (II) and Co (III) acetylacetonates, nickel (II) acetyl acetate, the derivatives of the carboxylic organic acids having, for example, 1-20 carbon atoms per molecule, such as nickel naphthenates, nickel 2-ethylhexanoate, nickel dimethyloctate, nickel benzoate, nickel stearate, nickel oleate, nickel trimethylheptanoate, cobalt 2-ethylhexanoate, cobalt naphthenates, cobalt linoleate, cobalt oleate, cobalt orthotoluate, cobalt palmitate, cobalt stearate, cobalt dimethyloctate, iron naphthenates, iron acetylacetonate, iron stearate, and iron octoate.

The organoaluminum derivative has the formula $AlR' R'' R'''$ in which the radicals R' , R'' and R''' , which may be identical or different, represent hydrogen or hydrocarbon radicals, each containing, for example, 1-20 carbon atoms. One can cite the following compounds: trimethylaluminum, triethylaluminum, tri-isobutylaluminum and diisobutylaluminum hydride.

The molar ratio between the metal derivative and the organoaluminum derivative is between 1:1 and 1:100, preferably between 1:1 and 1:50.

One can prepare the catalyst starting at ordinary temperature, but catalysts which are prepared at temperatures of up to 200°C are still very active.

The catalytic solution can be used without special precautions, in particular, without aging. In general, the solution is immediately injected after its preparation.

While the organoaluminum derivative can be used either in pure or diluted form in tetrahydronaphthalene up to concentrations of 0.01 mol/L, the metal derivative is used in

solution in tetrahydronaphthalene at concentrations between 0.01 mol/L and saturation at the temperature of the preparation of the catalysts.

After the interaction of the two constituents of the catalyst, the ratio of the volume of the catalytic solution to the volume of the reactants to be treated in continuous or batch mode operation can be between 1:1000 and 1:5, preferably between 1:500 and 1:10.

The preparation can be carried out in the presence of a gas, such as argon, nitrogen, methane or hydrogen, or in a mixture of these constituents. It is not necessary for the purity of this gas to be high.

Similarly, tetrahydronaphthalene can contain naphthalene up to the quantity corresponding to saturation at the temperature of preparation of the catalysts and small quantities of decahydronaphthalene up to 5%, preferably less than 1%.

The hydrogenation reaction can be carried out at temperatures between 20 and 250°C, preferably between 100 and 200°C. The concentration of metal in the metal derivative can vary between 0.0001 and 1 wt%, preferably between 0.001 and 0.1 wt%.

The partial pressure of hydrogen can vary between 0.1 and 100 bar, and preferably between 1 and 50 bar.

The naphthalene can be used in pure form or diluted in an inert solvent such as saturated hydrocarbons, or tetrahydronaphthalene.

After the reaction, the catalyst can be separated from the tetrahydronaphthalene produced by distillation, washing or simple percolation through a bed of absorbent consisting of silica gel, alumina, silica, bleaching earth, activated charcoal, etc.

The method can be carried out either in batch mode or continuously. In the latter case, the operation is preferably carried out in two reactors, one operating at a stationary concentration of 70-98%, the other with a gradient which allows purifying the tetrahydronaphthalene to a specified degree which can be as high as 99%, and even 99.9%.

If necessary, one can use two reactors with stationary concentration instead of one.

The following examples illustrate the invention without limiting it:

Example 1 – One introduces 750 g naphthalene in a 1-L autoclave. One introduces hydrogen, and one raises the temperature to 210°C. One introduces the catalyst formed from the interaction of 5 mmol nickel 2-ethylhexanoate and 15 mmol triethylaluminum in solution in tetrahydronaphthalene. The hydrogen pressure is raised to 70 bar, and one allows the reaction to continue for 10 min. One recovers the tetrahydronaphthalene which contains 0.05% naphthalene and 1% decahydronaphthalene.

Example 2 – For comparison, one operates as in Example 10, test 7, of French Patent 1390 570 with 2.5 mol% nickel 2-ethylhexanoate in benzene: at 210°C, at a hydrogen pressure of

70 bar, and after a reaction time of 10 min, the conversion rate is only 10%. After complete conversion of the naphthalene, after 12 h, the effluent has the following composition:

Naphthalene	0.05
Tetrahydronaphthalene	86.95
Decahydronaphthalene	11.00
Various	2.00

These two examples are good illustrations of the greater activity and the better selectivity of the catalyst prepared according to the invention.

Examples 3-11 – One operates as in Example 1.

	① Sels métalliques	② Composés aluminiques	t°C	pression bars	durée hr	⑤ % poids Composition de l'effluent		
						N	T	D
3	Stéarate de Nickel 5 mmols ⑥	Al(Ethyl) ₃ 20 mmols	150	3	8	-	99	7
4	Stéarate de Fer 5 mmols ⑦	Al(Ethyl) ₃ 20 mmols	150	3	30	20	80	-
5	Acétylacétonate de Co (II) 5 mmols ⑧	Al(Méthyl) ₃ 15 mmols	150	10	6	0,1	99,8	0,1
6	Acétylacétonate de Co (III) 5 mmols ⑨	Al(Ethyl) ₃ 25 mmols	150	10	8	0,1	99	0,9
7	Stéarate de Cobalt 5 mmols ⑩	AlH(isobutyl) ₂ 15 mmols	150	30	3	-	98	2
8	Octoate de Cobalt 5 mmols ⑪	Al(isobutyl) ₃ 20 mmols	200	10	8	-	97	3
9	Naphténate de Nickel 8 mmols ⑫	AlH(isobutyl) ₂ 35 mmols	170	3	10	-	95	5
10	Stéarate de Cobalt 1 mmol ⑩	Al(éthyl) ₃ 4 mmols	120	30	15	0,3	99	0,7
11	Naphténate de Cobalt 8 mmols ⑬	Al(éthyl) ₃ 35 mmols	170	5	10	0,1	99,5	0,4
N : naphtalène T : tétrahydronaphtalène D : décahydronaphtalène ⑭								

- Key:
- 1 Metal salts
 - 2 Aluminum compounds
 - 3 Pressure bar
 - 4 Duration h
 - 5 wt%
 - Composition of the effluent
 - 6 Nickel stearate
 - 7 Iron stearate
 - 8 Co (II) acetylacetonate

- 9 Co (III) acetylacetonate
- 10 Cobalt stearate
- 11 Cobalt octoate
- 12 Nickel naphthenate
- 13 Cobalt naphthenate
- 14 N: naphthalene
T: tetrahydronaphthalene
D: decahydronaphthalene

Claims

1. Method for the hydrogenation in the liquid phase of naphthalene to tetrahydronaphthalene, by means of gaseous hydrogen, characterized in that one operates in the presence of a catalytic system which is soluble in the reactants to be treated, which comprise:
 - a) a salt of a transition metal of group VIII,
 - b) an organoaluminum derivative having the formula $AlR' R'' R'''$ in which the radicals R' , R'' and R''' , which may be identical or different, represent hydrogen or hydrocarbon radicals, each containing, for example, 1-20 carbon atoms, and
 - c) tetrahydronaphthalene.
2. Method according to Claim 1, in which the transition metal is iron, cobalt or nickel.
3. Method according to Claim 1 or 2, in which the transition metal is acetylacetonate.
4. Method according to Claim 1 or 2, in which the salt of the transition metal is a salt of a C_1 - C_{20} carboxylic organic acid salt which is soluble in tetrahydronaphthalene.
5. Method according to one of Claims 1-4, in which the alkylaluminum salt is triethylaluminum.
6. Method according to Claim 1, in which the hydrogenation temperature is 100-200°C.
7. Method according to Claim 1, in which the concentration of the metal derivative in the reactants to be hydrogenated is 0.001-0.1 wt%.
8. Method according to Claim 1, in which the partial pressure of hydrogen is 0.1-100 bar.
9. Method according to Claim 1, in which one operates in at least one reactor with a gradient.
10. Method according to Claim 1, in which the ratio of the volume of the catalytic solution introduced to the volume of the reactants to be treated is between 1:500 and 1:10.
11. Method according to Claim 1, in which the catalyst is used without prior aging.
12. Tetrahydronaphthalene obtained by the method of one of Claims 1-11.